



## Bioleaching of zinc and manganese from spent Zn–Mn batteries and mechanism exploration

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### ABSTRACT

In this work, bioleaching was used to extract valuable Zn and Mn from spent Zn–Mn batteries. The results showed that 96% of Zn extraction was achieved within 24 h regardless of energy source types and bioleaching bacteria species. However, initial pH had a remarkable influence on Zn release, extraction dose sharply decreased from 2200 to 500 mg/l when the initial pH value increased from 1.5 to 3.0 or higher. In contrast to Zn, all the tested factors evidently affected Mn extraction; the maximum released dose of 3020 mg/l was obtained under the optimum conditions. The acidic dissolution by biogenic H<sub>2</sub>SO<sub>4</sub> by the non-contact mechanism was responsible for Zn extraction, while Mn extraction was owed to both contact/biological and non-contact mechanisms. The combined action of acidic dissolution of soluble Mn<sup>2+</sup> by biogenic H<sub>2</sub>SO<sub>4</sub> and reductive dissolution of insoluble Mn<sup>4+</sup> by Fe<sup>2+</sup> resulted in 60% of Mn extraction, while contact of microbial cells with the spent battery material and incubation for more than 7 days was required to achieve the maximum extraction of Mn.

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### 1. Introduction

The consumption of batteries has increased sharply in the last 30 years because of the versatility, low maintenance, reduced cost and their requirements by the electronics industry (De Souza et al., 2001). Disposal of spent batteries represents a growing environmental problem due to the metallic content, being considered as hazardous waste (Sayilgan et al., 2009a). The Zn–Mn batteries, including alkaline and zinc–carbon batteries, are used in radios, recorders, toys, remote controls, watches, calculators, cameras and in many other objects where small quantities of power are required (Sayilgan et al., 2009a). It is estimated that the Zn–Mn batteries occupy over 90% of the total annual sales of portable batteries due to their low prices, especially in the developing countries like China. Usually, they are run out rapidly and thrown away (Bartolozzi, 1990). As a special residue containing mercury, zinc, manganese and other heavy metals, the waste batteries cause a serious concern due to their toxicity, abundance and permanence in the environment (Li and Xi, 2005).

Although many of alkaline and zinc–carbon batteries still are landfilled or incinerated, instead of being collected and recycled (De Michelis et al., 2007); more and more countries have published new regulations to prohibit the ultimate disposal of portable,

industrial and automotive batteries and accumulators by incineration or landfill regardless of their shape, volume, weight, material composition or use (Sayilgan et al., 2009a). Due to the rising demand and limited natural resources supply, many valuable metals including manganese and zinc have been listed as the strategic metals by many countries (Kim et al., 2009). The typical metal composition of alkaline and zinc–carbon batteries is that the Zn and Mn contents are about 12–28% and 26–45% of the total powder mass, respectively; the remaining components mainly include graphite, K and Fe which are cheap, abundant and nontoxic (Sayilgan et al., 2009a). Therefore, recycling processes for spent zinc–carbon and alkaline–manganese batteries should be developed to achieve environmental conservation as well as the effective utility of resources in terms of such high contents of valuable Zn and Mn (Kim et al., 2009).

In the last two decades, several processes have been developed to recycle the spent batteries as a result of new environmental regulations around the world (Veloso et al., 2005). Pyrometallurgical processes are the most used processes for the recycling of batteries, consisting basically of selective volatilization of metals at elevated temperatures followed by condensation (De Michelis et al., 2007). Pyrometallurgical routes do not require battery dismantling and are relatively simple processes; however, operations are very energy consuming and extremely harsh, equipment requirement is high, emissions of dust and gases are expected which require dust collecting/gas cleaning systems, and they are

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not versatile (Nogueria and Margarido, 2004). Hydrometallurgical techniques are becoming a well-established and efficient method for recovering metals from raw materials, characterized by different steps of pre-treatment followed by leaching and separation of different metals by electrolysis, extraction or precipitation (Sayilgan et al., 2009a). Compared with pyrometallurgical routes, hydrometallurgical ones have some inherent advantages including relatively simpler operation, less energy demand and no gas emissions (Sayilgan et al., 2009b).

Acid leaching of spent Zn–Mn batteries by hydrometallurgical processes mostly harvests 100% of extraction yield for Zn, but the release efficiency was rather low for Mn, being 10–40% (Sayilgan et al., 2009a). Moreover, the heavy consumption of strong acid such as  $H_2SO_4$ , HCl and  $HNO_3$  endows the leaching process with high cost, strict equipment requirement and potentially safe risk (Sayilgan et al., 2009a). Although reductive acid leaching can greatly improve extraction efficiency of Mn in the presence of  $H_2O_2$  or  $SO_2$  (Kim et al., 2009; Senanayake et al., 2010), the massive application of the dangerous and harmful reductive inorganic matter brings additional safety risk to the hydrometallurgical processes. The use of organic acids as reductants to replace the dangerous and harmful reductive inorganic matter can alleviate the potential risk (Sayilgan et al., 2010), but an increase in operation cost is inevitable. Therefore, development of environmental friendly and cost-effective recycling methods for the spent Zn–Mn batteries should be encouraged (Sayilgan et al., 2009a).

In the mining industry, the bio-hydrometallurgical processes (bioleaching) have been gradually replacing hydrometallurgical ones due to their higher efficiency, lower cost and few industrial requirements (Rossi, 1990; Das et al., 2011; Liu et al., 2011a,b). Bioleaching generally allows efficient release of metals from solid phase into aqueous solution under mild conditions such as room temperature and pressure in the presence of acidophilic sulfur-oxidizing and iron-oxidizing bacteria (Rohwerder et al., 2003; Cui and Zhang, 2008). On a resource management level, spent batteries could be considered as a source of secondary raw materials (Ferella et al., 2008). Recently, bioleaching processes for recovering valuable metals Co, Li, Ni, Cd from spent nickel–cadmium batteries and lithium ion batteries as the secondary batteries have attained significant attentions (Cerruti et al., 1998; Zhao et al., 2008; Mishra et al., 2008; Xin et al., 2009), displaying great application potential. However, there are few reports associated with the bioleaching of spent Zn–Mn batteries for the recovery of valuable metals Zn and Mn.

In this work, the bioleaching was used for extraction of Zn and Mn from spent Zn–Mn batteries. The extraction yield of both Zn and Mn by different bioleaching bacteria under various energy source types was compared; the difference regarding extraction behavior and mechanism between Zn and Mn was unveiled. Both of these works were carried out for the first time.

## 2. Methods

### 2.1. Batteries dismantling, powder preparation and content measurement for Zn and Mn

The spent alkaline and zinc–carbon batteries were manually dismantled. Dismantling products such as ferrous scraps, zinc rolled tins, copper caps, carbon rod, plastic films and paper pieces were removed. The powders, which were about 40–64% of the total weights of dismantling batteries (Sayilgan et al., 2010), were mixed, dried, ground by milling and sieved to obtain a mesh size of less than 200  $\mu m$  (Mishra et al., 2008). The resulting powder was used for bioleaching experiments. Prior to experiments, the contents of both Zn and Mn in the powder were determined as

230 and 310 g/kg, respectively, using atomic absorption spectrophotometer after digestion by  $HF-HNO_3-HCl$  method (USEPA, 1995).

### 2.2. Microorganisms and media

The *Alicyclobacillus* sp. as sulfur-oxidizing bacteria and the *Sulfobacillus* sp. as iron-oxidizing bacteria were used for bioleaching of spent Zn–Mn batteries in the form of either individual or mixed in the present work. Elemental sulfur and  $FeSO_4$  were utilized as energy sources to grow the *Alicyclobacillus* sp. and the *Sulfobacillus* sp. for regular maintenance and inoculums, respectively. The detailed procedures and methods about screen, culture, maintenance, inoculums and identification of the sulfur-oxidizing bacteria and the iron-oxidizing bacteria were described in the previous paper (Xin et al., 2009, 2011). The bioleaching media were prepared by adding different energy substrates, elemental sulfur, pyrite or the combined, into the basic medium containing  $(NH_4)_2SO_4$ , 2.0 g;  $KH_2PO_4$ , 1.0 g;  $MgSO_4 \cdot 7H_2O$ , 1.0 g;  $CaCl_2$ , 0.25 g;  $FeSO_4 \cdot 7H_2O$ , 0.18 g; distilled water, 1000 ml.

### 2.3. Bioleaching of spent Zn–Mn batteries by different bioleaching bacteria

The bioleaching media containing a mixed energy source of 2.0 g/l elemental sulfur and 2.0 g/l pyrite were prepared and placed into 250 ml flasks at a portion of 100 ml per flask. The sulfur-oxidizing bacteria *Alicyclobacillus* sp. only at 10% (v/v), the iron-oxidizing bacteria *Sulfobacillus* sp. only at 10% (v/v), or both of them at 5% (v/v) for each as mixed culture were inoculated respectively into the flasks containing bioleaching media and incubated in a shaker at 30 °C at 120 rpm. After 8–10 days culture, with the mixed culture the pH value of bioleaching media decreased to ca. 1.5 (Flasks A), with the sulfur-oxidizing bacteria dropped to about 1.7 (Flasks B), with the iron-oxidizing bacteria declined to around 1.9 (Flasks C). At that moment the pH value of Flasks B and C was adjusted precisely to the same value (ca. 1.5) as Flasks A with 0.5 mol/l  $H_2SO_4$  solution, and then 1 g of powder batteries materials was added into Flasks A, B and C, respectively. The flasks containing battery materials were continuously incubated in the shaker to carry out bioleaching. During bioleaching, the oxidation–reduction potential (ORP) value and the pH value of the solutions were monitored; the dissolved doses of both Zn and Mn were measured for analyzing the extraction yield. Sterile controls were performed in the absence of bacteria using filter-sterilized medium at initial pH of 5.5 or after the  $H_2SO_4$  adjust to pH 1.5 synchronized with the above-mentioned Flasks A, B and C. All the experiments, including the sterile controls, were carried out in triplicates.

### 2.4. Bioleaching of spent Zn–Mn batteries under different energy sources

The different bioleaching media containing 4.0 g/l elemental sulfur, 4.0 g/l pyrite, or 2.0 g/l elemental sulfur + 2.0 g/l pyrite as energy sources were prepared and placed into 250 ml flasks at a portion of 100 ml per flask. Both the *Alicyclobacillus* sp. and the *Sulfobacillus* sp. at 5% (v/v) for each as mixed culture were inoculated respectively into the flasks and incubated in a shaker at 30 °C at 120 rpm. After 8–10 days incubation, the pH value of bioleaching media containing 4.0 g/l elemental sulfur decreased to ca. 1.5 (Flasks D), with 2.0 g/l elemental sulfur + 2.0 g/l pyrite dropped to about 1.6 (Flasks E), with 4.0 g/l pyrite declined to around 1.8 (Flasks F). At that moment the pH value of Flasks E and F was adjusted precisely to the same value (ca. 1.5) as Flasks D with  $H_2SO_4$  solution, and then 1 g of batteries materials was added into Flasks D, E and F. The batteries materials-contained

flasks were continuously incubated in the shaker to carry out the bioleaching. In the course of bioleaching, the released concentrations of both Zn and Mn, the ORP value and the pH value of the bioleaching media were monitored. Suitable controls were performed as described above. All the experiments, including the controls, were carried out in triplicates.

### 2.5. Bioleaching of spent Zn–Mn batteries under different initial pH

Both the *Alicyclobacillus* sp. and the *Sulfobacillus* sp. were inoculated respectively at 5% (v/v) into the 100 ml of bioleaching media containing 2.0 g/l elemental sulfur + 2.0 g/l pyrite as energy source in the 250 ml flasks and were incubated in the shaker. After 8–10 days culture, the pH value of media decreased to ca. 1.5. The flasks without pH adjustment were designated as Flasks G, the flasks adjusted to pH 3.0 with 0.5 mol/l NaOH solution were designated as Flasks H, the flasks adjusted to pH 4.5 were designated as Flasks I. One gram of powder batteries materials was added into Flasks G, H and I, followed by continuously incubation in the shaker for the bioleaching. The released doses of Zn and Mn, the ORP value and the pH value of the bioleaching media were detected. Suitable controls were run in the course of bioleaching and all the experiments were carried out in triplicates.

### 2.6. Contact or non-contact bioleaching mechanisms exploration

One gram of powder batteries material was encapsulated in a small dialysis bag, and then placed and divided into the bioleaching media containing 2.0 g/l elemental sulfur + 2.0 g/l pyrite, when the pH value of the media dropped to about 1.5 by the mixed culture of the sulfur-oxidizing bacteria and the iron-oxidizing bacteria after 8–10 days incubation (Flasks J). The free batteries material also underwent the same bioleaching process as the encapsulated ones as a contrast (Flasks K). The extraction behavior of Zn and Mn as well as the variation pattern of pH value and ORP value between Flasks J and Flasks K was compared during bioleaching through periodical sample and measurement. The suitable controls were run and all the experiments were carried out in triplicate. The experiments principle and detailed procedures were available in previous paper (Xin et al., 2009).

### 2.7. XRD, SEM and EDX analysis of the powder batteries material before and after bioleaching by the mixed culture in the presence of elemental sulfur and pyrite

After bioleaching experiments, the batteries material residues in the dialysis bag from Flasks J were collected, washed and dried. The leached residues were analyzed by XRD, SEM and EDX and compared with the original sample. The experiments principle and detailed procedures were available in previous paper (Xin et al., 2009).

### 2.8. Distribution analysis of Zn and Mn before and after bioleaching under the mixed energy sources by the mixed culture using the sequential extraction procedures

After bioleaching experiments, the batteries material residues in the dialysis bag from Flasks J were collected, washed and dried. The distribution of Zn and Mn of the leached batteries residues was analyzed using the improved BCR sequential extraction procedures and compared with the original sample. The exact experiment procedures were available in the literature (Rauret et al., 1999).

### 2.9. Chemical simulation of bioleaching process by the mixed culture in the presence of both elemental sulfur and pyrite as mixed energy sources

The dissolution behavior of Zn and Mn from the powder batteries material in Flasks L containing 100 ml of 4.0 g/l  $\text{Fe}^{2+}$ - $\text{H}_2\text{SO}_4$  combined solution (pH 1.5), in Flasks M containing 100 ml of 4.0 g/l  $\text{Fe}^{3+}$ - $\text{H}_2\text{SO}_4$  combined solution (pH 1.5) was compared with that in Flasks N containing 100 ml of  $\text{H}_2\text{SO}_4$  solution only at same pH value. 1.0 g of the batteries material was placed into the above-mentioned Flasks L, M and N. The extracted content of Zn and Mn into solution as well as the pH and ORP value of solution was monitored periodically in the process of leaching. All the experiments were conducted in triplicates. The experiments principle and detailed procedures were available in previous paper (Xin et al., 2009).

### 2.10. Apparatuses and condition

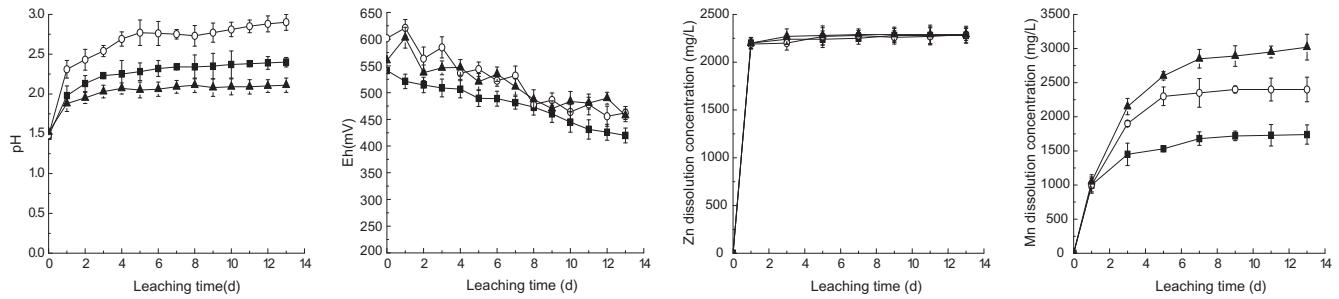
The pH value of bioleaching media was determined using a precise pH meter, the ORP value was determined by portable ORP meter; the released dose of Zn and Mn was determined by atomic absorption spectrophotometer (361MC, Shanghai Precision Scientific Instrument Co. Ltd., China). Morphological changes of batteries residues after bioleaching were analyzed by using scanning electron microscope (SEM, Hitachi S-4800, Japan) at an accelerating voltage of 20 kV. Micro-area chemical analysis was performed by energy dispersive X-ray analysis (EDX, Oxford) operating at 20.0 keV. Structure change analysis was performed by X-ray diffractometer (XRD, Shimadzu) with Cu Ka radiation ( $k = 1.5418$ ).

## 3. Results and discussion

### 3.1. Bioleaching of spent Zn–Mn batteries by different bioleaching bacteria

The released concentrations of both Zn and Mn, pH value and ORP value of the three leaching bacteria systems as a function of bioleaching time were presented in Fig. 1. Variation of bioleaching bacteria had no effect on dissolution of Zn; 2200 mg/l of extraction dose and 96% of extraction efficiency were attained within 24 h of contact regardless of bioleaching bacteria species, displaying the rapid extraction property of bioleaching for Zn from the spent Zn–Mn batteries. In contrast to Zn, Mn bioleaching was a relatively slow release process and the maximum extraction doses of Mn were obtained after 13 days of incubation. Moreover, different leaching bacteria exhibited different extraction ability of Mn. The mixed culture harvested the highest extraction concentration of 3020 mg/l, i.e. 97% of extraction yield; whilst the sulfur-oxidizing bacteria only resulted in the lowest extraction of 1740 mg/l, equivalent to 56% of extraction yield.

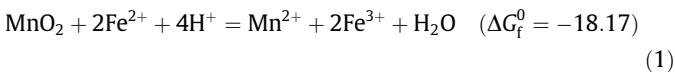
In the spent Zn–Mn batteries, Zn usually existed in the form of  $\text{ZnO}$ ; Mn generally existed in the form of  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  (Sayilgan et al., 2009a).  $\text{ZnO}$  was readily soluble in sulfuric, hydrochloric and nitric acid; however, acidic dissolution of  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  was partial, because the produced  $\text{MnO}_2$  was insoluble (Sayilgan et al., 2009a). For extraction of  $\text{Zn}^{2+}$  from sewage sludge, a threshold of pH value at ca. 4.9 was required (Villar and Garcia, 2002). In the mixed culture system, the iron-oxidizing bacteria oxidized  $\text{FeS}_2$  to produce  $\text{Fe}^{3+}$  which further chemically reacted with  $\text{FeS}_2$  to release elemental sulfur (Xin et al., 2009). The resulting sulfur along with the added one was oxidized by the sulfur-oxidizing bacteria to generate more  $\text{H}_2\text{SO}_4$ , leading to the lowest pH value at ca. 2.1 which ensured complete acid dissolution of Zn from the batteries materials. In contrast, the sole iron-oxidizing bacteria system



**Fig. 1.** Time-courses for pH value, ORP value, Zn extraction dose, Mn extraction dose during bioleaching of spent Zn–Mn batteries by different bacteria under mixed energy sources (—■— sulfur-oxidizing bacteria, —○— iron-oxidizing bacteria, —▲— mixed culture).

harvested the highest pH value of about 2.9 because of the poor oxidizing ability of sulfur. However, the rapid release of Zn was still observed at pH 2.9 since it was yet much lower than the threshold value of 4.9 (Villar and Garcia, 2002). Therefore, different leaching bacteria systems yielded nearly 100% of Zn extraction, as an evidence for that Zn release from the spent Zn–Mn batteries was due to acid dissolution by the bio-genetic  $H_2SO_4$ .

Although the acid dissolution by bio-genetic  $H_2SO_4$  could also extract the  $Mn^{2+}$  from  $Mn_2O_3$  and  $Mn_3O_4$ , the  $Mn^{4+}$  in the form of residue  $MnO_2$  was resistant and insoluble (Sayilgan et al., 2009a). In the presence of the iron-oxidizing bacteria,  $FeS_2$  could be bio-chemically oxidized to generate  $H_2SO_4$ , accompanied with release of biogenic  $Fe^{2+}$ ; on the other hand, the biogenic  $Fe^{3+}$  from bio-oxidation of  $Fe^{2+}$  triggered a series of chemical reactions to produce chemical origin  $Fe^{2+}$  (Xin et al., 2009). The biogenic  $Fe^{2+}$  along with the chemical origin  $Fe^{2+}$  reduced insoluble  $Mn^{4+}$  into soluble  $Mn^{2+}$  in the presence of  $H^+$  as below:



As a result, both iron-oxidizing bacteria system and mixed culture system exhibited higher extraction efficiency of Mn than the sulfur-oxidizing bacteria system due to the reduction of insoluble  $Mn^{4+}$  into soluble  $Mn^{2+}$  by  $Fe^{2+}$ , reflected by the strong fluctuation in ORP during bioleaching. Furthermore, the lower pH value in mixed culture system promoted stronger generation of  $Fe^{3+}$  than iron-oxidizing bacteria system (Xin et al., 2009). As a result, more  $Fe^{3+}$  led to greater production of  $Fe^{2+}$  which strongly accelerated the reduction of  $Mn^{4+}$  and extraction of resulting  $Mn^{2+}$ . Therefore, the mixed culture system resulted in the highest Mn extraction. As the extraction of Mn was a resultant of both acidic dissolution and reduction of  $Fe^{2+}$ , the release of Mn by bioleaching was slower than that of Zn with sole acidic dissolution.

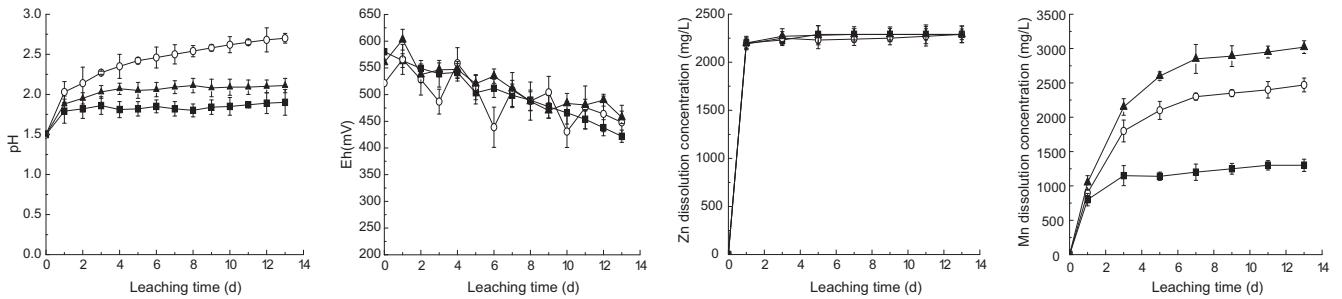
### 3.2. Bioleaching of spent Zn–Mn batteries under different energy sources

The released concentrations of both Zn and Mn, pH value and ORP value as function of leaching time under three energy sources were presented in Fig. 2. Energy sources types also had no effect on extraction of Zn; no matter in the elemental sulfur system with the lowest pH value of ca. 1.9 or in the pyrite system with the highest pH of about 2.7, the extraction concentration of Zn rapidly reached 2200 mg/l after 24 h of bioleaching. It was because that the Zn was readily released from the spent Zn–Mn batteries in the form of  $ZnO$  in the case of pH value below 4.9 (Villar and Garcia, 2002). Although sulfur that existed in the form of pyrite was more difficult to be bio-oxidized into  $H_2SO_4$  than the elemental sulfur by the mixed culture, leading to the highest pH of about 2.7 in the pyrite leaching system; it still assured the same rapid and complete release of Zn as in the other leaching systems.

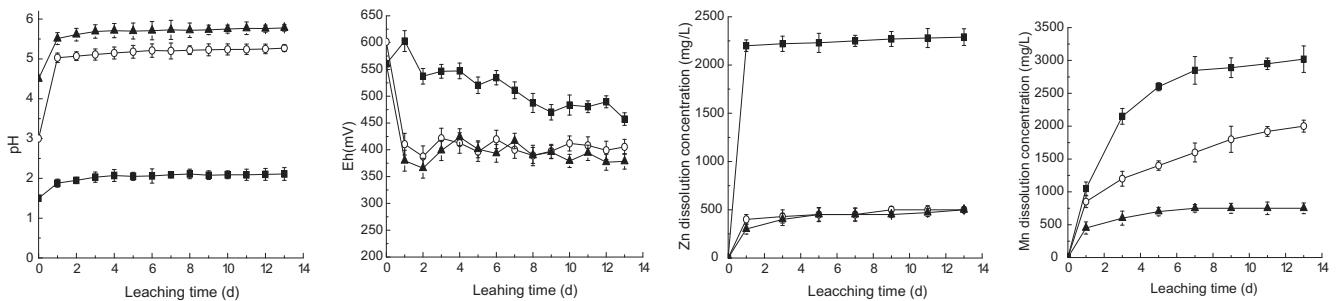
Unlike Zn, the energy sources types had a great influence on the extraction efficiency of Mn. The elemental sulfur system harvested the lowest extraction performance of Mn and the released concentration reached 1300 mg/l after 13 days contact despite of the lowest pH value; whilst the mixed energy sources system of sulfur + pyrite resulted in the highest extraction efficiency and the released dose reached a maximum of 3020 mg/l after the same period of bioleaching. The extraction efficiency of Mn in the mixed energy sources system was 2.3 times as high as that in the sulfur system. With sulfur being the sole energy source, acidic dissolution was the dominant mechanism for bioleaching, leading to the release of soluble  $Mn^{2+}$  from batteries material (Xin et al., 2009). Using pyrite as the sole energy source, the biogenic  $Fe^{3+}$  triggered a series of chemical reactions to produce  $Fe^{2+}$  which reduced insoluble  $Mn^{4+}$  into soluble  $Mn^{2+}$ , leading to the release of insoluble  $Mn^{4+}$  (Xin et al., 2009); the oxidation–reduction reaction between  $Mn^{4+}$  and  $Fe^{2+}$  was reflected by the fierce fluctuation in ORP value during bioleaching. Using sulfur + pyrite as the mixed energy sources, both strongly acidic dissolutions of soluble  $Mn^{2+}$  by  $H_2SO_4$  from bio-oxidation of elemental sulfur and reduction dissolution of insoluble  $Mn^{4+}$  by  $Fe^{2+}$  mainly from chemical reactions triggered by biogenic  $Fe^{3+}$ , were responsible for the extraction of Mn from the spent Zn–Mn batteries (Xin et al., 2009), leading to the best bioleaching performance of Mn.

### 3.3. Bioleaching of spent Zn–Mn batteries under different initial pH

The released concentrations of both Zn and Mn, pH value and ORP value as function of leaching time under different initial pH were presented in Fig. 3. The initial pH had a remarkable influence on the extraction performance of both Zn and Mn. With increase of initial pH value from 1.5 to 4.5, the maximum extraction dose of Mn decreased almost linearly from 3020 to 750 mg/l after incubation of 13 days. In contrast with Mn, the maximum extraction dose of Zn was 2200 mg/l at initial pH of 1.5; however, when the initial pH value increased to 3.0 or higher, the maximum extraction doses sharply declined to less than 500 mg/l. In the case of the initial pH value of 1.5, the pH of bioleaching media initially rose due to massive release of KOH in battery material and then kept almost unchanged at about 1.9 showing the balance between consumption of  $H_2SO_4$  for acid dissolution and production of bio-genetic  $H_2SO_4$ , allowing complete acidic extraction of Zn. However, with the initial pH value of 3.0 or 4.5, the pH value of bioleaching media sharply rose to above 4.9 as threshold for Zn dissolution, leading to very poor Zn extraction. On the other hand, although different initial pH values permitted the reduction of insoluble  $Mn^{4+}$  by  $Fe^{2+}$  into soluble  $Mn^{2+}$  reflected by the fluctuation in ORP value during bioleaching, the final dissolution of  $Mn^{2+}$  into aqueous solution was strongly dependant on the pH value of leaching media. Therefore, the initial pH almost linearly determined the extraction concentration of Mn. The results exhibited the huge function of acidic dissolution in the bioleaching of the spent batteries.



**Fig. 2.** Time-courses for pH value, ORP value, Zn extraction dose, Mn extraction dose during bioleaching of spent Zn–Mn batteries under different energy sources by mixed culture (—■— elemental sulfur; —○— pyrite; —▲— mixed energy sources).



**Fig. 3.** Time-courses for pH value, ORP value, Zn extraction dose, Mn extraction dose during bioleaching of spent Zn–Mn batteries under different initial pH value using mixed energy sources by mixed bacteria (—■— pH 1.5; —○— pH 3.0; —▲— pH 4.5).

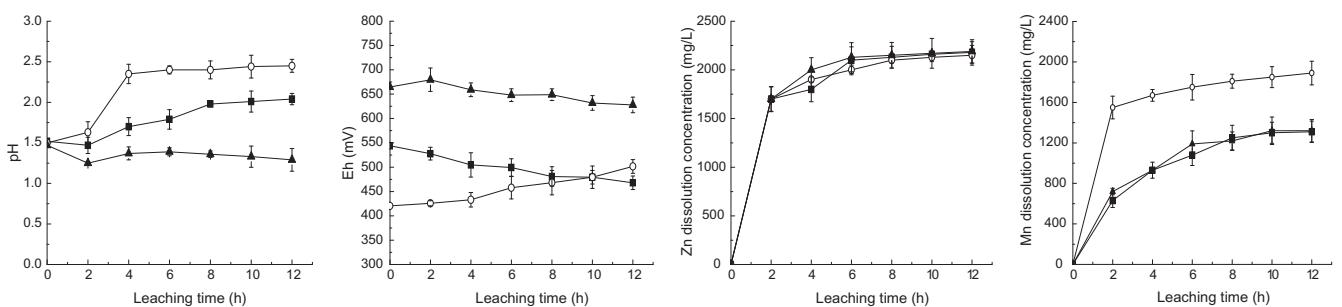
### 3.4. Chemical simulation of bioleaching process by the mixed culture

Based on the bioleaching experiments as presented above, it was deduced that in the bioleaching system using elemental sulfur and pyrite as the mixed energy sources by the mixed culture displaying the best extraction performance of the batteries, the extraction of Zn was carried out owing to the acidic dissolution by the bio-genetic  $H_2SO_4$ ; whilst the release of Mn was due to the combined action of acidic dissolution of soluble  $Mn^{2+}$  by the biogenetic  $H_2SO_4$  and reduction dissolution of insoluble  $Mn^{4+}$  by the  $Fe^{2+}$  from chemical reactions triggered by biogenetic  $Fe^{3+}$ . In order to further determine the role of  $H^+$ ,  $Fe^{2+}$  and  $Fe^{3+}$  in the extraction of Zn and Mn from the spent batteries, chemical simulation of bioleaching process was conducted (Fig. 4).

It was found that the  $H_2SO_4$  only extracted about 2180 mg/l of Zn after 12 h of contact and addition of  $Fe^{2+}$  or  $Fe^{3+}$  did not affect the release efficiency of Zn; although the existence of  $Fe^{3+}$  resulted in a slight drop in pH value due to the hydrolysis and the addition of  $Fe^{2+}$  caused a weak rise in pH value due to oxidization of  $Fe^{2+}$  into  $Fe^{3+}$ , accompanied by consumption of  $H^+$ . The results fully demonstrated that the extraction of Zn was independent of the

oxidation–reduction reaction relating to  $Fe^{2+}/Fe^{3+}$ . Furthermore, it was concluded that the acidic dissolution by biogenic  $H_2SO_4$  as the non-contact mechanism was responsible for the extraction of Zn from the spent batteries by the bioleaching based on the fact that the released dose of Zn (2180 mg/l) in the chemical leaching system was almost equal to that (2200 mg/l) in the bioleaching system.

Like Zn, the addition of  $Fe^{3+}$  did not improve the extraction performance of Mn compared with the sole  $H_2SO_4$  chemical leaching system and a released dose of 1320 mg/l was attained after 12 h of contact; however, the existence of  $Fe^{2+}$  evidently promoted the extraction efficiency of Mn, resulting in 1890 mg/l of extracted dose and continued increase in ORP value owing to the generation of  $Fe^{3+}$  from  $Fe^{2+}$  oxidation in the  $H_2SO_4$ – $Fe^{2+}$  leaching system. This demonstrated that the reduction dissolution of insoluble  $Mn^{4+}$  into soluble  $Mn^{2+}$  by  $Fe^{2+}$  as non-contact mechanism really occurred in the course of bioleaching. However, the much higher released dose of Mn (3020 mg/l) in the bioleaching system than that (1890 mg/l) in the chemical leaching system indicated that other unknown contact or non-contact mechanisms may have occurred in the bioleaching system, besides the combined action of acidic dissolution



**Fig. 4.** Variations of pH value, ORP value, Zn extraction dose, Mn extraction dose as a function of time during leaching of the spent Zn–Mn batteries by different chemical leaching systems simulating bioleaching processes (—■—  $H^+$ ; —○—  $H^+-Fe^{2+}$ ; —▲—  $H^+-Fe^{3+}$ ).

of soluble Mn<sup>2+</sup> by the biogenetic H<sub>2</sub>SO<sub>4</sub> and reduction dissolution of insoluble Mn<sup>4+</sup> by the Fe<sup>2+</sup> as non-contact mechanism.

### 3.5. Contact or non-contact bioleaching mechanisms exploration

In order to further distinguish the roles of contact and non-contact mechanisms in bioleaching of the spent batteries, the dissolution behavior of Zn and Mn between material inside a dialysis bag (trapped) and free in solution (not trapped) was compared. It was found that there was almost no difference in the dissolution behavior of Zn between trapped and non-trapped conditions, suggesting that the non-contact mechanism of acidic dissolution by biogenic H<sub>2</sub>SO<sub>4</sub> was the sole reason for the extraction of Zn. As for Mn, however, that was a completely different case. The encapsulation of batteries materials greatly reduced the extraction dose of Mn from 3010 to 1860 mg/l, indicating that a certain contact mechanism might occur in the bioleaching system which needed to be studied further, beyond the acidic dissolution by biogenic H<sub>2</sub>SO<sub>4</sub> and reduction dissolution by the Fe<sup>2+</sup> as non-contact mechanism.

### 3.6. Distribution analysis of Zn and Mn before and after bioleaching

In order to eliminate the interference of the energy substrates on the analysis of batteries material, the batteries residual after bioleaching by the non-contact mechanism was collected from the dialysis bag which received the improved BCR sequential extractions according to the method of Rauret et al. (1999) and then compared with the raw batteries material (Table 1). It was found that Zn existed mainly in the form of weak acid soluble fraction (52%) and Fe–Mn oxide/hydroxide bound fraction (39%) in the raw batteries material; the Zn was almost completely extracted after bioleaching by the non-contact mechanism, leaving 3% in the residual. As for Mn, it existed mainly in the form of Fe–Mn oxide/hydroxide bound fraction (58%) and weak acid soluble fraction (23%); after bioleaching by the non-contact mechanism, weak acid soluble fraction and Fe–Mn oxide/hydroxide bound fraction was extracted to 97% and 58%, respectively, having 24% of extraction yield for sulfide bound fraction and no extraction for residual fraction. The total remaining Mn (40%) in the residual could be released by certain unidentified way as contact mechanism due to having 97% of extraction yield in the case of non-trapped.

### 3.7. XRD, SEM and EDX analysis of batteries material before and after bioleaching

The batteries residual after bioleaching by the non-contact mechanism was collected from the dialysis bag and analyzed by XRD, SEM and EDX and compared with the raw batteries material. The SEM analysis showed that the border of the powder batteries material grew blurred after bioleaching, indicating that leaching process was still ongoing. The surface analysis of EDX displayed that Zn was released completely after bioleaching, while Mn evi-

dently remained in the residual due to the non-contact mechanism. The spot analysis of EDX further revealed that the remaining Mn existed in the form of manganese oxide due to only appearance of peaks representing manganese and oxygen. The XRD analysis demonstrated that the MnO<sub>2</sub> occurred as the existed form of Mn in the residual after bioleaching by the non-contact mechanism, whilst it existed in the form of Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> in the raw sample. As for Zn, it was almost completely released after bioleaching as was showed by the disappearance of the peak representing Zn compound.

In the presence of only non-contact mechanism with the dialysis bag, Zn was almost completely extracted by acid dissolution of biogenic H<sub>2</sub>SO<sub>4</sub>, while 62% of released efficiency was attained for Mn by combined action of acidic dissolution by biogenic H<sub>2</sub>SO<sub>4</sub> and reduction dissolution by the Fe<sup>2+</sup>. However, in the case of non-trapped, in which both contact and non-contact mechanisms worked, Mn harvested as high as 97% of extraction yield, suggesting the great potential of bioleaching in releasing both Mn and Zn from the spent Zn–Mn batteries. The hydrometallurgical processes using strong acid harvested almost 100% of extraction yield for Zn, but the release efficiency of Mn was often 10–40% (Sayilgan et al., 2009a). Although the addition of H<sub>2</sub>O<sub>2</sub>, SO<sub>2</sub> or organic acids as reductants could evidently improve the extraction efficiency of Mn, the potential safety risk grew higher and the leaching cost rose up significantly (Kim et al., 2009; Senanayake et al., 2010; Sayilgan et al., 2010). In contrast, bioleaching process not only was efficient in extraction of Zn and Mn from the spent batteries, but also recognized as economical, safe, environmental friendly one.

## 4. Conclusions

Bioleaching extracted 96% of Zn within 24 h regardless of energy source types and bioleaching bacteria species. However, only the mixed culture using mixed energy sources assured the maximum extraction of 97% for Mn after 13 days. The sole acidic dissolution by biogenic H<sub>2</sub>SO<sub>4</sub> as the non-contact mechanism was responsible for extraction of Zn; while the 97% of extraction yield for Mn was due to both contact mechanism and non-contact one. The combined action of acidic dissolution of soluble Mn<sup>2+</sup> by biogenic H<sub>2</sub>SO<sub>4</sub> and reduction dissolution of insoluble Mn<sup>4+</sup> by Fe<sup>2+</sup> as non-contact mechanism resulted in just 60% of extraction yield.

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**Table 1**  
Distribution analysis of both Zn and Mn of the spent Zn–Mn batteries before and after bioleaching by the improved BCR sequential extractions (mg/l).

Metal types	Zn		Mn		
	Sample types	Raw sample	BCR Leached	Raw sample	BCR Leached
Weak acid soluble fraction	1180 ± 104	6 ± 6	730 ± 83	23 ± 12	
Fe–Mn oxide/hydroxide bound fraction	880 ± 92	17 ± 4	1840 ± 107	780 ± 94	
Sulfide bound fraction	170 ± 21	22 ± 6	290 ± 41	219 ± 36	
Residual fraction	24 ± 3	26 ± 11	326 ± 62	367 ± 22	

Note: The BCR sequential extraction procedures described by Rauret et al. (1999) were used to leach the battery material.

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